



Global emission inventories for C₄–C₁₄ perfluoroalkyl carboxylic acid (PFCA) homologues from 1951 to 2030, part II: The remaining pieces of the puzzle



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ABSTRACT

We identify eleven emission sources of perfluoroalkyl carboxylic acids (PFCAs) that have not been discussed in the past. These sources can be divided into three groups: [i] PFCAs released as ingredients or impurities, e.g., historical and current use of perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA) and their derivatives; [ii] PFCAs formed as degradation products, e.g., atmospheric degradation of some hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs); and [iii] sources from which PFCAs are released as both impurities and degradation products, e.g., historical and current use of perfluorobutane sulfonyl fluoride (PBSF)- and perfluorohexane sulfonyl fluoride (PHxSF)-based products. Available information confirms that these sources were active in the past or are still active today, but due to a lack of information, it is not yet possible to quantify emissions from these sources. However, our review of the available information on these sources shows that some of the sources may have been significant in the past (e.g., the historical use of PFBA-, PFHxA-, PBSF- and PHxSF-based products), whereas others can be significant in the long-term (e.g., (bio)degradation of various side-chain fluorinated polymers where PFCA precursors are chemically bound to the backbone). In addition, we summarize critical knowledge and data gaps regarding these sources as a basis for future research.

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Terminology

1. The emission inventory of C₄–C₁₄ perfluoroalkyl carboxylic acid (PFCA) homologues is compiled by investigating the fate of certain chemical species during the life-cycle of relevant products. The products are grouped and named after their major ingredients, e.g. products containing perfluorooctanoic acid (PFOA) and its derivatives that have the same functional moiety (i.e. the perfluoroalkane carbonyl moiety, C_nF_{2n+1}C(O)-; including salts, esters, etc.; hereafter denoted by *derivatives*) as major ingredients are categorized as PFOA-based products. The same terminology is used for other products presented in this paper. In addition to those species that are intentional ingredients in products, [i] PFCAs and their derivatives as undesired byproducts (hereafter *impurities*) and [ii] unreacted raw materials (hereafter *residuals*) in products are also accounted for in the inventory.
2. PFCA sources are divided into two categories. *Direct* sources include PFCA emissions from the life-cycle of [i] PFCA-based products that contain PFCAs or their derivatives as major ingredients and [ii] other products in which PFCAs and/or their derivatives are present as impurities. *Indirect* sources refer solely to formation of PFCAs from degradation of precursors in the environment and biota. In this work we adopt the terminology proposed by Buck et al. (2011), which is slightly different from that used by Prevedouros et al. (2006), regarding whether PFCA impurities in other products are considered as direct (here) or indirect sources (by Prevedouros et al., 2006).
3. PFCAs and their perfluoroalkane sulfonyl fluoride (PASF)- and fluorotelomer-based precursors belong to the chemical class known as poly- and perfluorinated alkyl substances (PFASs). PFASs are chemicals that contain one or more perfluoroalkyl moieties, –C_nF_{2n+1} (Buck et al., 2011). In the past, PFASs were often referred to as “PFCs” (per- and polyfluorinated chemicals), but this acronym is also often used for perfluorocarbons; perfluorocarbons contain only carbon and fluorine and have properties and functionalities different from those of PFASs.

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1. Introduction

Long-chain perfluoroalkyl carboxylic acids (PFCAs, $C_nF_{2n+1}COOH$, $n \geq 7$), including perfluorooctanoic acid (PFOA or C_8 PFCA) and perfluorononanoic acid (PFNA or C_9 PFCA), have attracted attention as global contaminants because of their persistence (Frömel and Knepper, 2010; Parsons et al., 2008; Vaalgamaa et al., 2011; Young and Mabury, 2010), bioaccumulation potential (Conder et al., 2008; ECHA, 2013), and global presence in the abiotic environment (Rayne and Forest, 2009), biota (Giesy and Kannan, 2001), food items (Gebbink et al., 2013; Picó et al., 2011) and humans (Vestergren and Cousins, 2009). In the European Union, C_{11} – C_{14} PFCAs are classified as very persistent and very bioaccumulative (vPvB) substances and PFOA and its ammonium salt (APFO) are classified as persistent, bioaccumulative and toxic (PBT) substances. These PFCA homologues have therefore been added to the Candidate List of Substances of Very High Concern (SVHC) under the European chemical regulation, REACH (EG 1907/2006) (ECHA, 2013).

For over a decade, numerous efforts have been made to study the origins of PFCAs in the environment. As a result, various sources have been identified, including emissions during the life-cycle (production, use and disposal) of products containing mainly [i] PFOA or its derivatives (PFOA-based products), [ii] PFNA or its derivatives (PFNA-based products), [iii] compounds derived from perfluorooctane sulfonyl fluoride (POSF-based products), and [iv] fluorotelomer-based derivatives (fluorotelomer-based products) (Prevedouros et al., 2006). The improved understanding of PFCA emission sources has enabled elucidations of the levels and trends of PFCAs in certain environments (Cousins et al., 2011). For example, indirect sources such as atmospheric transport and degradation of POSF- and fluorotelomer-based derivatives are important origins of PFCAs in remote inland ecosystems (Ellis et al., 2004) such as the Arctic ice caps (Schenker et al., 2008; Young et al., 2007) or alpine lakes (Benskin et al., 2011), whereas direct sources (such as fluoropolymer production sites) contribute significantly to the overall presence of PFOA and PFNA in the oceans on a global scale (Armitage et al., 2006, 2009a,b; Prevedouros et al., 2006; Schenker et al., 2008; Stemmler and Lammel, 2010; Wania, 2007). However, the understanding of the origins of PFCAs in the environment is still incomplete. For example, the updated global emission inventory of C_4 – C_{14} PFCA homologues based on the sources listed above cannot

explain the reported, surprisingly high levels of some (especially short-chain) PFCA homologues monitored in open ocean surface water (see section *Comparison to estimated ocean inventory* in the companion paper) (Wang et al., 2014).

In this study, we identify eleven new PFCA sources that (might) emit PFCAs [i] as ingredients or impurities (i.e., direct sources), [ii] as degradation products (i.e., indirect sources), and [iii] as impurities and degradation products (i.e., direct and indirect sources). Due to a lack of quantitative information (e.g., production volume, usage, and/or degradation half-lives and yields), these newly identified sources cannot be included in the quantitative global emission inventory described in the companion paper (Wang et al., 2014). However, these sources may constitute important contributions to historical and/or future PFCA emissions. We summarize available information on these sources and highlight critical knowledge/data gaps in the *Newly identified, but currently unquantifiable sources* section, so as to provide an up-to-date overall picture of the sources of PFCAs in the environment and to highlight future research needs (e.g., identification of overlooked point sources or human exposure routes). We further perform a bounding analysis in order to elaborate if and when (bio)degradation of POSF- and fluorotelomer-based side-chain fluorinated polymers can be a relevant source of PFCAs. Information on specific substances mentioned in this work was retrieved from a review of publicly available information and no substance identified in the literature review process was disregarded. The list of substances here expands the previous knowledge on the sources of PFCA homologues, however, the list itself is by no means complete; further studies on identifying (new) sources are needed.

2. Newly identified, but currently unquantifiable sources

In addition to the four PFCA sources that were summarized and quantified by Prevedouros et al. (2006) and in our companion paper (Wang et al., 2014) with important updates and amendments (see Fig. 1, left column), we have identified eleven more sources (see Fig. 1, right column). Details on these sources are provided in the next subsections; critical knowledge and data gaps regarding each source are summarized in Table 1.

Emissions of PFCAs and their derivatives

Quantified sources	Currently unquantifiable sources
<p>A. as ingredients or impurities / direct sources</p> <ol style="list-style-type: none"> 1. historical and current use of APFO/NaPFO as processing aids in the (emulsion) polymerization of PTFE, FEP, PFA and PVDF; 2. historical and current use of APFN as processing aids in the emulsion polymerization of PVDF. <p>for details: see Wang et al. (2014)</p>	<ol style="list-style-type: none"> 1. historical use of PFOA and its derivatives [i] as processing aids in the polymerization of fluoroelastomers, [ii] surface treatment of textile, leather and paper, [iii] as fluorinated surfactants in various products (such as AFFFs), etc.; 2. historical (and current) use of APFN in fluorinated surfactants; 3. possible use of branched PFNA between the 1960s and early 1990s 4. historical and current use of PFBA, PFHxA and their derivatives; 5. historical use of PFDS that contains PFCAs as impurities.
<p>B. as degradation products / indirect sources</p>	<ol style="list-style-type: none"> 1. atmospheric degradation of hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs); 2. possible formation of PFCAs during the thermolysis of fluoropolymers such as PTFE in municipal waste incinerators or at industrial recycling sites; 3. possible biodegradation of POSF- and fluorotelomer-based side-chain fluorinated polymers;
<p>C. as impurities and degradation products</p> <ol style="list-style-type: none"> 1. historical and current use of chemicals derived from POSF; * 2. historical and current use of n:2 FT-based substances; * <p>* PFCAs are emitted as impurities (in both side-chain fluorinated polymers and non-polymers-based products) & degradation products of non-polymeric substances.</p> <p>for details: see Wang et al. (2014)</p>	<ol style="list-style-type: none"> 1. historical and current use of chemicals derived from PBSF and PhxSF, where PFCAs can be emitted as impurities and degradation products; 2. historical and current use of semifluorinated alkanes, where PFCAs can be emitted as impurities and degradation products; 3. historical and current use of n:1 FT-based substances, where PFCAs can be emitted as impurities and degradation products;

Fig. 1. Overview of identified sources of perfluoroalkyl carboxylic acids (PFCAs) and their derivatives in the environment. Left: sources that have been quantified by Prevedouros et al. (2006) and by Wang et al. (2014). Right: sources that are newly identified but currently cannot be quantified. APFO/NaPFO = ammonium/sodium salts of perfluorooctanoic acid (PFOA), APFN = ammonium salt of perfluorononanoic acid (PFNA), PTFE = polytetrafluoroethylene, FEP = fluorinated ethylene-propylene copolymers, PFA = perfluoroalkoxy polymers, PVDF = polyvinylidene fluoride, AFFF = aqueous film-forming foam, PFBA = perfluorobutanoic acid, PFHxA = perfluorohexanoic acid, PFDS = perfluorodecane sulfonic acid, POSF = perfluorooctane sulfonyl fluoride, FT = fluorotelomer, PBSF = perfluorobutane sulfonyl fluoride, PhxSF = perfluorohexane sulfonyl fluoride.

Table 1

Critical data gaps that currently prevent quantification of newly identified sources.

Available information	Critical knowledge and data gaps
1. Historical use of PFOA and its derivatives for use other than in fluoropolymer production [i] chemical composition of products and uses	[i] volume of production and emissions; [ii] PFCA homologue compositions
2. Historical use of PFNA and its derivatives for use other than in PVDF production [i] evidence of use from monitoring data	[i] chemical compositions and details of use; [ii] volume of production and emissions; [iii] PFCA homologue compositions
3. Historical use of branched PFNA and its derivatives [i] evidence of use from patents and monitoring data	[i] chemical compositions and detailed uses; [ii] volume of production and emissions; [iii] PFCA homologue compositions
4. Historical and current use of PFBA, PFHxA and their derivatives [i] production/import ranges in the US in some years; [ii] historical use of PFBA; [iii] current use of PFHxA and some derivatives	[i] chemical compositions and other use; [ii] volume of production and emissions; [iii] PFCA homologue compositions
5. Historical use of PFDS that contains PFCAs as impurities [i] production/import ranges in the US in some years; [ii] use as ingredients in floor polishes	[i] volume of production, other uses and emissions; [ii] PFCA impurity levels; [iii] PFCA homologue compositions
6. Atmospheric transformation of hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs) [i] likely transformation mechanism; [ii] laboratory-measured kinetic rate constants	[i] volume of production, uses and emissions; [ii] yields of PFCA homologue formation; [iii] extrapolation factor (laboratory → field)
7. possible thermolysis of fluoropolymers such as PTFE [i] likely transformation mechanism	[i] yields of PFCA homologue formation; [ii] volume of PFCAs released
8. (Bio)degradation of POSF- and fluorotelomer-based side-chain fluorinated polymers [i] laboratory measured biodegradation half-lives of some fluorotelomer-(methyl)acrylate-based side-chain fluorinated polymers	[i] volume of production, use and emissions of different types; [ii] realistic degradation half-lives; [iii] yields of PFCA homologue formation
9. Historical and current use of chemicals derived from PBSF and PHxSF [i] current use of some PBSF/PHxSF-based derivatives [ii] transformation mechanism of some derivatives	[i] chemical compositions and detailed use; [ii] volume of production and emissions; [iii] impurity levels of PFCA homologues; [iv] extrapolation factor (laboratory → field)
10. Historical and current use of semifluorinated alkanes [i] evidence of PFCAs as impurities; [ii] likely transformation mechanism	[i] volume of production, uses and emissions; [ii] impurity levels of PFCA homologues; [iii] half-lives and yields of PFCA homologue formation
11. Historical and current use of n:1 FT-based substances [i] laboratory-measured transformation mechanism and kinetic rate constants	[i] volume of production, uses and emissions; [ii] impurity levels of PFCA homologues; [iii] yields of PFCA homologue formation; [iv] extrapolation factor (laboratory → field)

2.1. Sources where PFCAs are emitted as ingredients or impurities (direct sources)

In addition to the ammonium or sodium salts that are used as processing aids in the (emulsion) polymerization of certain fluoropolymers, PFOA-based products were or have been used as processing aids in the polymerization of fluoroelastomers such as base-resistant elastomers (CAS Nos. 54675-89-7 and 27029-05-6) and CTFE elastomers (CAS No. 9010-75-7) (Millet, 2005; Willis, 2007). By 2004 3M/Dyneon had stopped its use of PFOA in the polymerization of CAS Nos. 54675-89-7 and 9010-75-7 as well as its import and sale of CAS No. 27029-05-6; by 2006 Asahi had ceased its use of APFO in the polymerization of CAS No. 27029-05-6 (Millet, 2005; Willis, 2007). In addition, APFO may also have been used in the polymerization of some other fluoroelastomers (CAS Nos. 9011-17-0, 25190-89-0, and 26425-79-6) manufactured by Daikin (Dai-el®), DuPont (Viton®) and Solvay (formerly Ausimont; Tecnoflon®) (Duncan, 2003; Kirk-Othmer, 2000; Yamashita et al., 2004).

However, PFOA-based products were also used in several other applications (see white boxes in Fig. 2). Before POSF-based replacements were commercialized, PFOA-based chromium complexes were used as oil- and water-repellent finishes for paper (e.g. FC-805, CAS No. 55801-89-3) and

stain-repellent finishes for leather (e.g. FC-146, CAS No. 37317-76-3) (Bryce, 1964; Philips et al., 1957; Scherer, 1970; Segal et al., 1958). PFOA derivatives (CAS Nos. 335-90-0, 5158-52-1 and 802270-49-1) were used as intentional ingredients in the early generation(s) of AFFFs (Francen, 1972; Turve and Jablonski, 1966). Small amounts of PFOA were also directly used as an antistatic additive in some medical film applications (3M, 2003), and as a surfactant in various products (e.g. cleaning formulations) (OECD, 2009; Scherer, 1970). In addition, PFOA was used as a starting material to produce an odd carbon-numbered fluorotelomer alcohol (n:1 FTOH, $C_nF_{2n+1}CH_2OH$), which will be discussed in detail below in Section 2.3. There is no detailed information on the production history of these uses, except that the global sales of PFOA and derivatives by 3M for non-fluoropolymer uses were about 6 tonnes per year (t/yr) between the late 1990s and early 2000s (FMG, 2002).

Similarly, PFNA-based products were also marketed and used as fluorinated surfactants (Buck et al., 2011), as indicated by monitoring data obtained from sampling and analyzing effluents from a metal-plating factory (US EPA, 2009) and a textile factory (Clara et al., 2008). Most of the historical PFNA and its derivatives were produced as linear isomers. However, several companies, notably Pennwalt and Daikin, developed techniques based on perfluoroisopropyl iodide and thus may

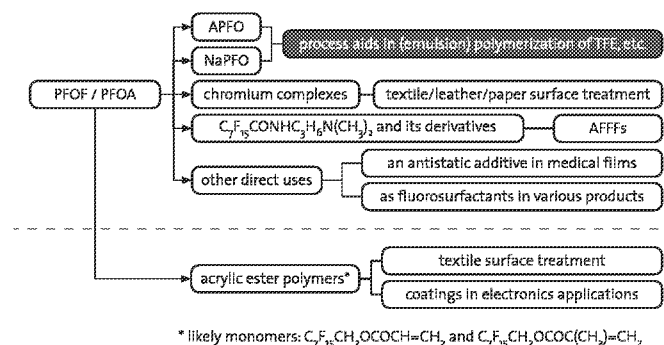


Fig. 2. Historical and current uses of PFOA and its derivatives, PFOA = perfluorooctanoic acid, which is the parent compound of PFOA. The black box represents the PFOA sources that have been quantified in the companion paper (Wang et al., 2014).

have manufactured branched PFNA-based products between the 1960s and early 1990s (Banks et al., 1994; Fielding, 1979). This intentional production of isopropyl PFNA is supported by detection of only the isopropyl PFNA but no other branched isomers in ringed seals from Resolute Bay and a single polar bear from the Canadian Arctic (De Silva et al., 2009).

C_4 – C_7 perfluoroalkane carbonyl fluorides (PACFs, $C_nF_{2n+1}COF$, $n = 3$ – 6), the raw materials used for production of the corresponding PFCAs or their derivatives, were already produced or imported in the United States (US) in the 1980s or even earlier in amounts exceeding 4.54 t/yr (see Table 2) (US EPA, 2013), principally through electrochemical fluorination (ECF). Among C_4 – C_7 PACF-based derivatives, some limited information on the historical and current use is available only for perfluorobutanoic acid (PFBA), perfluorohexanoic acid (PFHxA) and derivatives.

PFBA was previously produced by 3M for use in photographic films, which ceased in 1998 due to decreasing customer demand (3M, 2008). After 2000, production of perfluorobutane carbonyl fluoride (PFBF) was revived by the same company (see Table 2) (US EPA, 2013); however, it is unknown whether PFBF has been used, as previously, to produce PFBA and its derivatives. In addition, Miteni has marketed PFBA and its methyl ester (CAS No. 356-24-1) for unknown use (Miteni, 2013).

The historical uses of PFHxA and its derivatives remain unidentified. Some fluoropolymer or fluoroelastomer producers, however, may have started to use PFHxA-derivatives to replace PFOA and PFNA as processing aids in the polymerization process (Iwai, 2011; Matsuoka and Watanabe, 2010), as recently observed at one production site in France (Dauchy et al., 2012). In addition, Miteni has marketed PFHxA, its ammonium salt (APFHx), its methyl ester (CAS No. 424-18-0) and $CF_3(CF_2)_4CONH(CH_2)_3Si(OCH_3)_3$ (CAS No. 154380-34-4, used in surface treatment of glasses, natural stones, metals, wood, cellulose, cotton, leather and ceramics) (Miteni, 2013). The current production of PFHxA and its derivatives may involve producers using oxidation of fluorotelomer raw materials (Kishikawa et al., 2009) and ECF (Miteni, 2013).

Perfluorodecane sulfonyl fluoride (PDSF) was also produced/imported by 3M in the US in the 1980s or even earlier (see Table 2) (US EPA, 2013). In 2002, 3M ceased its global production of PDSF-based chemistry (3M, 2000a). PDSF has likely only been used as an intermediate to produce the ammonium salt of perfluorodecane sulfonic acid (NH_4 -PFDS), which was used as a wetting and leveling agent in consumer products such as floor polishes (3M, 2000b). During ECF of decanesulfonyl fluoride to PDSF, some perfluoroalkyl chains are likely unintentionally reacted to PACFs through the electrochemical oxidation and are subsequently hydrolyzed to PFCAs by moist air or in the subsequent reactions, as occurred during the ECF of octanesulfonyl fluoride to POSF (Gramstad and Haszeldine, 1957). Thus, PFCAs and their derivatives were likely present as impurities in NH_4 -PFDS-containing consumer products and may have been released into the environment during the product life-cycle.

2.2. Sources where PFCAs are emitted as degradation products (indirect sources)

An indirect source of PFCAs that has not been discussed up to now is the atmospheric transformation of certain volatile hydrofluorocarbons (HFCs) and hydrofluoroethers (HFEs) to PFCAs. In the early 1990s, due to their near-zero ozone depletion potential, HFCs started to be applied as replacements of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which contribute to the depletion of stratospheric ozone (Tsai, 2005a). However, due to their significant global warming potential, several HFCs are considered to be target greenhouse gases under the United Nations Framework Convention on Climate Change (UNFCCC, 2013). Hence, HFEs have been developed to replace HFCs since the middle 1990s (Tsai, 2005b, 2009). Several HFCs and HFEs have been identified to be potential precursors of C_4 – C_{11} PFCAs (see Table 3).

Among HFCs, those with the $-CHF_2$, $-CH_2F$, $-CH_3$ or $-C_2H_5$ moiety at the end of a perfluoroalkyl chain may undergo a series of atmospheric reactions and partially form PFCAs (mechanisms of atmospheric formation of PFCAs have been summarized in a recent review by Young and Mabury (2010)):

- [i] HFCs with the $-CHF_2$ moiety (e.g., HFC-329cc and HFC 52-13p) can react with OH radicals and form a perfluoroalkyl radical $[CF_3(CF_2)_n\cdot]$, which can further react to form PFCAs (under low NO_x conditions) (Chen et al., 2004, 2011a; Young et al., 2009).
- [ii] HFCs with the $-CH_2F$ moiety (e.g., CF_3CH_2F) can undergo a series of reactions with OH radicals, O_2 and NO, and yield an alkoxy radical [e.g., $CF_3C(O\cdot)HF$], which can either react with O_2 and yield $CF_3C(O)F$ or decompose and form $HC(O)F$ and $\cdot CF_3$ (Rattigan et al., 1994). The authors noted that the reaction of the alkoxy radical with O_2 is favored with decreasing temperature and pressure (e.g., at high altitudes and latitudes) (Rattigan et al., 1994).
- [iii] HFCs with the $-CH_3$ moiety (e.g., CF_3CH_3) can react with OH radicals to produce fluorinated alkyl radicals (e.g., $CF_3CH_2\cdot$) that can further react with O_2 to give peroxy radicals (e.g., $CF_3CH_2O_2\cdot$) (Nielsen et al., 1994). The peroxy radical reacts with NO and forms $-CH_2O\cdot$ radicals, which react with O_2 to give the $-C(O)H$ moiety (Nielsen et al., 1994). The $-C(O)H$ moiety can undergo reaction with OH radicals to yield perfluoroacyl radicals [e.g., $CF_3C(O)\cdot$], which can either react with O_2 to give a $[CF_3(CF_2)_nC(O)OO\cdot]$ radical or lose carbon monoxide to give a perfluoroalkyl radical $[CF_3(CF_2)_n\cdot]$ (Young and Mabury, 2010). In addition, $CF_3(CF_2)_nC(O)H$ can undergo photolysis to give a perfluoroalkyl radical $[CF_3(CF_2)_n\cdot]$ (Young and Mabury, 2010). Both $CF_3(CF_2)_nC(O)OO\cdot$ and $CF_3(CF_2)_n\cdot$ are known PFOA precursors (Young and Mabury, 2010).
- [iv] HFCs with the $-C_2H_5$ moiety ($C_nF_{2n+1}CH_2CH_3$) can likely react with OH radicals and form two types of radicals, i.e. $C_nF_{2n+1}CH_2CH_2\cdot$ and $C_nF_{2n+1}CH(\cdot)CH_3$, (for an example of n -butane see Atkinson, 1986). $C_nF_{2n+1}CH_2CH_2\cdot$ radicals can likely undergo a series of reactions with O_2 and NO and form $C_nF_{2n+1}CH_2CH_2O\cdot$ (i.e. $C_nF_{2n+1}CH_2CH_2\cdot \rightarrow C_nF_{2n+1}CH_2CH_2O_2\cdot \rightarrow C_nF_{2n+1}CH_2CH_2O\cdot \rightarrow C_nF_{2n+1}CH_2C(O)H$; similarly to $CF_3CH_2\cdot \rightarrow CF_3CH_2O_2\cdot \rightarrow CF_3CH_2O\cdot \rightarrow CF_3C(O)H$ in Nielsen et al., 1994). Similarly, $C_nF_{2n+1}CH(\cdot)CH_3$ can likely undergo a series of reactions with O_2 and NO and yield $C_nF_{2n+1}CH(O\cdot)CH_3$, which can either decompose to form $C_nF_{2n+1}\cdot$ and CH_3CHO or further react with O_2 and form $C_nF_{2n+1}C(O)CH_3$ (for an example of $CH_3CH_2CH(\cdot)CH_3$ see Atkinson, 1986). $C_nF_{2n+1}C(O)CH_3$ can likely further undergo a series of reactions and give $C_nF_{2n+1}C(O)OO\cdot$ (similarly to $CF_3C(O)CH_3 \rightarrow CF_3C(O)OO\cdot$ in Carr et al., 2003). $C_nF_{2n+1}CH_2C(O)H$, $CF_3(CF_2)_nC(O)OO\cdot$ and $CF_3(CF_2)_n\cdot$ are all known PFOA precursors (Young and Mabury, 2010).

Most of the studies on the OH radical-mediated transformation of the HFCs mentioned above were made for homologues with short

Table 2

Reported production/import volume ranges of C₄–C₈ PACFs and PFCAs as well as C₄–C₈ and C₁₀ PASFs and PFSAs in the US. All figures are retrieved from the US EPA CDR database (formerly Inventory Update Reporting (IUR) database) (US EPA, 2013).

Chemicals	CAS number	Reporting year production/import volume range in the US [t/yr]					
		1986	1990	1994	1998	2002	2006
PFBF	335-42-2	4.54–227	N.R.	4.54–227	454–4540	454–4540	454–4540
PFPeF	375-62-2	N.R.	4.54–227	N.R.	N.R.	N.R.	N.R.
PFHpF	375-84-8	N.R.	4.54–227	N.R.	N.R.	N.R.	N.R.
PFOF	335-66-0	4.54–227	4.54–227	4.54–227	4.54–227	N.R.	<227
PFBA	375-22-4	4.54–227	N.R.	N.R.	N.R.	N.R.	N.R.
APFHx	21615-47-4	N.R.	N.R.	4.54–227	4.54–227	N.R.	N.R.
PFOA	335-67-1	4.54–227	N.R.	4.54–227	4.54–227	4.54–227	<227
APFO	3825-26-1	4.54–227	4.54–227	4.54–227	4.54–227	4.54–227	<227
APFN	72623-77-9	N.R.	N.R.	N.R.	N.R.	4.54–227	N.R.
APFN	72968-3-88	N.R.	4.54–227	N.R.	4.54–227	N.R.	N.R.
PBSF	375-72-4	4.54–227	4.54–227	4.54–227	4.54–227	4.54–227	227–454
PPeSF	375-81-5	4.54–227	4.54–227	4.54–227	4.54–227	N.R.	N.R.
PHxSF	423-50-7	4.54–227	4.54–227	4.54–227	4.54–227	227–454	N.R.
PHpSF	335-71-7	4.54–227	4.54–227	4.54–227	4.54–227	N.R.	N.R.
POSF	307-35-7	454–4540	454–4540	454–4540	454–4540	4.54–227	N.R.
PDSF	307-51-7	N.R.	4.54–227	4.54–227	N.R.	N.R.	N.R.
K-PFBS	29420-49-3	4.54–227	4.54–227	4.54–227	4.54–227	4.54–227	<227
K-PFHxS	3871-99-6	N.R.	4.54–227	N.R.	N.R.	N.R.	N.R.
PFOs	1763-23-1	N.R.	N.R.	4.54–227	N.R.	4.54–227	N.R.
K-PFOs	2795-39-3	4.54–227	4.54–227	4.54–227	4.54–227	4.54–227	N.R.
NEt ₄ -PFOs	56773-42-3	N.R.	N.R.	N.R.	4.54–227	4.54–227	N.R.
NH ₄ -PFDS	67906-42-7	N.R.	4.54–227	4.54–227	4.54–227	4.54–227	N.R.

N.R. = not reported.

perfluoroalkyl chains and PFCA yields were not determined in these studies. Previous studies show that the OH radical reaction rate constant for CF₃CF₂CH₃ is about 20% higher than that for CF₃CH₃ (Orkin et al., 1997), whereas no clear trend of the OH radical reaction rate constants among CF₃(CF₂)₂CHF₂, CF₃(CF₂)₄CHF₂ and CF₃(CF₂)₆CHF₂ is observed (see Table 3). Therefore, it is unknown how changes in the perfluoroalkyl chain length influence the reaction kinetics and PFCA yields.

Among HFEs, HFE-7100 and 7200/8200 can react with OH radicals and form C₄F₉OC(O)H as well as C₄F₉OC(O)CH₃ and C₄F₉OC(O)H, respectively (Chen et al., 2011b; Christensen et al., 1998; Wallington et al., 1997). These intermediates can undergo further reaction with OH radicals and form PFBA (for a detailed mechanistic analysis, see Chen et al., 2011b). In addition, the atmospheric oxidation of HFE-7500 forms C₃F₇CF(OC(O)CH₃)/CF(CF₃)₂ and C₃F₇CF(OC(O)H)/CF(CF₃)₂ (Goto et al., 2002). The authors also suggested that both degradation

Table 3

Major hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs) and n:1 fluorotelomer alcohols (FTOHs) that can degrade into PFCAs along with their ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers) refrigerant designation or abbreviation (commercial name), CAS number (CAS No.), structure, rate constants for reaction with OH radicals at 298 K, if available, and end-products (we consider only C₄–C₁₄ PFCAs here). N.A. = not available.

ASHRAE code or abbreviation (commercial name)	CAS No.	Structure	$k_{(OH+R)}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Potential end-product(s)
HFC-347ccd	662-00-0	CF ₃ (CF ₂) ₃ CH ₃	N.A.	PFBA
HFC-338ccb	662-35-1	CF ₃ (CF ₂) ₂ CH ₂ F	N.A.	PFBA
HFC-329ccb	375-17-7	CF ₃ (CF ₂) ₂ CHF ₂	$1.85 \pm 0.29 \times 10^{-15} (296 \text{ K})^a$	PFBA
HFC 52-13p (AC-2000, TH-6)	355-37-3	CF ₃ (CF ₂) ₄ CHF ₂	$1.69 \pm 0.07 \times 10^{-15}$, $1.72 \pm 0.07 \times 10^{-15}$, $1.87 \pm 0.11 \times 10^{-15}$, $2.12 \pm 0.11 \times 10^{-15}$ b	C ₄ –C ₆ PFCAs
N.A. (TH-8)	335-65-9	CF ₃ (CF ₂) ₆ CHF ₂	$2.62 \pm 0.30 \times 10^{-15}$, $2.66 \pm 0.03 \times 10^{-15}$ c	C ₄ –C ₆ PFCAs
N.A. (TH-10)	375-97-3	CF ₃ (CF ₂) ₈ CHF ₂	N.A.	C ₄ –C ₁₀ PFCAs
HFC-569mccf (AC-4000, TEH-4)	38436-17-8	CF ₃ (CF ₂) ₃ CH ₂ CH ₃	N.A.	PFBA
HFC-76-13sf (AC-6000, TEH-6)	80793-17-5	CF ₃ (CF ₂) ₅ CH ₂ CH ₃	N.A.	C ₄ –C ₇ PFCAs
N.A. (TEH-8)	77117-48-7	CF ₃ (CF ₂) ₇ CH ₂ CH ₃	N.A.	C ₄ –C ₉ PFCAs
N.A. (TEH-10)	154478-87-2	CF ₃ (CF ₂) ₉ CH ₂ CH ₃	N.A.	C ₄ –C ₁₁ PFCAs
HFE-449mccc (HFE 7100)	163702-08-7 & 163702-07-6	75% (CF ₃) ₂ CF ₂ OC ₂ H ₅ & 25% CF ₃ (CF ₂) ₃ OC ₂ H ₅	-1.2×10^{-14} d, $7.2 \pm 1.6 \times 10^{-15}$ e, $1.48 \pm 0.07 \times 10^{-14}$ f, $1.49 \pm 0.13 \times 10^{-14}$ g	PFBA
HFE-569mccc (HFE 7200/8200)	163702-05-4 & 163702-06-5	(CF ₃) ₂ CF ₂ OC ₂ H ₅ & CF ₃ (CF ₂) ₃ OC ₂ H ₅	$1.00 \pm 0.03 \times 10^{-13}$ f, $7.32 \pm 0.55 \times 10^{-14}$ g	PFBA
N.A. (HFE-7500)	297730-93-9	C ₃ F ₇ CF(OC ₂ H ₅)/CF(CF ₃) ₂	$2.6 \pm 0.6 \times 10^{-14}$ h	PFBA
3:1 FTOH (RM 610)	375-01-9	C ₃ F ₇ CH ₂ OH	$1.02 \pm 0.10 \times 10^{-13}$ i, $1.07 \pm 0.05 \times 10^{-13}$ g	PFBA
5:1 FTOH (RM 620)	423-46-1	C ₅ F ₁₁ CH ₂ OH	N.A.	C ₄ –C ₆ PFCAs

a Young et al., 2009.

b Chen et al., 2004; kinetic rate constants for reaction with OH radicals were measured with four different methods in the same study.

c Chen et al., 2011a; kinetic rate constants for reaction with OH radicals were measured using CF₃CHF₂ and CF₃CH₂F as the reference substance, respectively.

d Wallington et al., 1997.

e Cavalli et al., 1998.

f Oyaro and Nielsen, 2003.

g Bravo et al., 2010.

h Goto et al., 2002.

i Hurley et al., 2004.

products will likely be hydrolysed by moist air and form $C_3F_7CF(OH)-CF(CF_3)_2$, which can likely be further oxidized to $C_3F_7C(O)CF(CF_3)_2$ (Goto et al., 2002). By analogy with the atmospheric degradation of $C_2F_5C(O)CF(CF_3)_2$ (Jackson et al., 2011), it is expected that $C_3F_7C(O)-CF(CF_3)_2$ can further undergo direct photolysis (under low NO_x conditions) or hydrolysis (rather slow) to yield PFBA.

It should be noted that all studies regarding HFCs and HFEs discussed above were conducted in the laboratory with zero or low levels of NO_x . In reality, when NO_x species are abundant, they may compete with those reactions that lead to formation of PFCAs, and thus lower the actual yields of PFCA formation in the environment. For example, the perfluoroalkyl radicals $[CF_3(CF_2)_n\cdot]$ react with NO to yield $[CF_3(CF_2)_{n-1}\cdot]$ and COF_2 and this reaction can continue until all perfluoroalkyl radicals are converted to COF_2 (Wallington et al., 2006). Hence, the actual degradation rate constants and PFCA yields in urban environments (where the NO_x levels can be high (mainly in the morning and evening) due to the traffic emissions; Filella and Peñuelas, 2006) are expected to be lower than observed in laboratory studies.

In addition to the highly uncertain degradation rate constants and PFCA yields, there has been only limited information on the historical and current global production and emissions of relevant HFCs and HFEs, preventing the quantification of PFCA emissions from atmospheric transformation of these substances. To our knowledge, some of the HFCs mentioned above have been commercialized as heat-transfer fluids, cleaning agents or solvents by (at least) Asahi and Fuxin Hengtong in China (their commercial names are listed in Table 3; Asahi, 2014; Fuxin, 2014). The amounts of these HFCs being produced and emitted remain unknown, except that $CF_3(CF_2)_5CH_2CH_3$ has been registered under REACH with annual production volumes of between one and ten tonnes (ECHA, 2014). HFE-7100, 7200/8200 and 7500 are marketed by 3M as heat transfer fluids and solvents for cleaning and coating (ECHA, 2014; Newsted et al., 2002; Sekiya et al., 2006; Tsai, 2005b; Wolf, 2011). In addition, HFE-7100 has been notified as a solvent for the manufacture of cosmetic products, including personal care products (skin, hair and bath care), fragrances and room scents in Australia and as CF-61 for cosmetic applications in the EU (NICNAS, 2006). They have been manufactured/imported in the US for more than a decade (see Table 4). Recently, HFE-7500 has also been registered under REACH with annual production volumes of more than ten tonnes (ECHA, 2014).

Another poorly-studied indirect source of PFCAs is the thermolysis of fluoropolymers such as PTFE. At appropriate temperatures (250–600 °C), fluoropolymers such as PTFE are capable of degrading predominantly to various monomers (C_2F_4 , C_3F_6 , C_4F_8 , etc.) (Ellis et al., 2001; Lewis and Naylor, 1947; Simon and Kaminsky, 1998; Sölch, 2012), which can react with air and partially form PFCAs of different chain lengths (Ellis et al., 2001; Sölch, 2012). Significant releases of PFCAs during cooking with PTFE-coated pans are unlikely at normal cooking temperatures (<230 °C; Coenders, 1992) (Imbalzano, 1991). It is unknown, however, to what extent these thermally induced transformations of

fluoropolymers may occur in municipal waste incinerators, where (i) flue gases reach higher temperatures (>850 °C, according to the EU Directive 2000/76/EC) and may result in different degradation products (García et al., 2007); (ii) other substances coexist and may interfere with the thermolysis of fluoropolymers (e.g., thermolysis of PTFE is inhibited by a hydrogen or chlorine atmosphere in contrast to steam, oxygen or sulfur dioxide, which accelerate decomposition; Simon and Kaminsky, 1998); and (iii) technologies such as activated carbon injection (ACI) coupled with baghouse filtration (BF) may be installed to remove dioxin or mercury and may also trap PFCAs (EU Commission, 2006). In 2005, the US EPA and four major fluoropolymer and fluoroelastomer producers (Asahi, Daikin, Dyneon and DuPont) reached an enforceable consent agreement (ECA) for a laboratory-scale incineration testing on fluoropolymers (US EPA, 2005). Results from an industry-sponsored study suggested that waste incineration of fluoropolymers does not emit detectable levels of PFOA under conditions representative of typical municipal waste combustor operations in the US (Taylor, 2009). To date, the final report of the ECA has not yet been published by the US EPA. Additionally, it is unclear to what extent PFCAs are formed and released at industrial recycling sites where fluoropolymer wastes are thermally decomposed to recycle monomers such as C_2F_4 and C_3F_6 (e.g., in mid-2012, Dyneon started construction of a pilot plant for the thermolysis of PTFE wastes (500 t/yr) at its Gendorf site in Germany; Dyneon, 2013).

The thermolysis of one type of side-chain fluorinated polymer, i.e., fluorotelomer-based acrylate polymer, has been studied and no formation of PFOA at temperatures between 600 and 1000 °C was observed (Yamada et al., 2005). Although thermolysis of side-chain fluorinated polymers is possibly an unimportant source of PFCAs, it has been reported that some side-chain fluorinated polymers (such as fluorotelomer-based acrylate polymer and urethane polymer) might degrade biotically to corresponding PFCA precursors (such as FTOHs) in aerobic soils (Russell et al., 2008, 2010a; Washington et al., 2009). A reliable estimation of the amount of PFCAs from (bio)degradation of side-chain fluorinated polymers is not yet possible, mainly because there is high uncertainty in the degradation half-lives (ranging from decades up to millennia) (Russell et al., 2010b; Washington et al., 2010), which is mostly due to the significant challenges associated with measuring such low degradation rate constants. It is also unknown to what extent laboratory conditions represent the real environment (in terms of temperature, bioavailability of polymers, microbial community, co-existence of other substances, etc.). In addition, many other types of side-chain fluorinated polymers than the ones tested are produced (Buck et al., 2011). It is unknown how their different physical and physicochemical properties would influence the bioavailability and thus the biodegradability. Below in Section 3, we perform a bounding analysis to evaluate whether (bio)degradation of side-chain fluorinated polymers can be a significant source of PFCAs in the long term.

2.3. Sources where PFCAs were/are emitted as impurities/residuals and degradation products (direct + indirect sources)

In addition to POSF, the shorter-chain homologues of perfluoroalkane sulfonyl fluorides (PASFs) and their derivatives were produced/imported by 3M in the US in the 1980s or even earlier (Table 2) (US EPA, 2013). Among these chemicals, information is available only on perfluorobutane sulfonyl fluoride (PBSF)- and perfluorohexane sulfonyl fluoride (PHxSF)-based derivatives. The historical use of PBSF-based derivatives remains unknown. Since 2002, they have been developed as replacements of their C_8 homologues in various industrial branches and are now produced in the US, Germany, Italy and China (Buck et al., 2011; Huang et al., 2010; Mitani, 2013; Möller et al., 2010; Wang et al., 2013). Information on production and uses of many PBSF-based derivatives (e.g., perfluorobutane sulfonic acid (PFBS), its salts and various PBSF-based side-chain fluorinated polymers) is provided in Wang et al.

Table 4

Reported production/import volume ranges of HFE-7100, 7200/8200 and 7500 in the US. All figures are retrieved from the US EPA CDR database (formerly Inventory Update Reporting (IUR) database) (US EPA, 2013).

Chemicals	CAS number	Reporting year production/import volume range in the US [t/yr]			
		1998	2002	2006	2013
HFE-7100	163702-08-7	454–4540	454–4540	454–4540	CBI
	163702-07-6	227–454	227–454	454–4540	CBI
HFE-7200/8200	163702-05-4	4.54–227	4.54–227	227–454	CBI
	163702-06-5	4.54–227	4.54–227	11.3–227	CBI
HFE-7500	297730-93-9	N.R.	4.54–227	11.3–227	CBI

N.R. = not reported; CBI = confidential business information.

(2013) and therefore not repeated here. In addition, we identify a new tetrabutyl phosphonium salt of PFBS ($(C_4H_9)_4P$ -PFBS, CAS No. 220689-12-3), which is used as an anti-static additive in plastics (ECHA, 2014; US EPA, 2012). In the US it has been produced by DuPont under the tradename Zonyl® FASP-1 (formerly FC-1) with a production volume of between 11.3 and 227 tonnes in 2005 (DuPont, 2007; US EPA, 2013), whereas in the EU it has been registered by Miteni under REACH with annual production volumes of more than 1 tonne per year (ECHA, 2014).

The production of PHxSF-based derivatives started in the 1960s, mainly for use in aqueous film-forming foams (AFFFs) that are used for fire-fighting purposes and in specific postmarket carpet treatment products (Olsen et al., 2003; Place and Field, 2012; Sundström et al., 2012; US EPA, 2013). In 2000–2002, 3M ceased its global production of PHxSF-based products parallel to the phase-out of its POSF-based products (3M, 2000a). However, some manufacturers in China and Italy have recently initiated the production of PHxSF-based products for use in, for example, textile finishing agents (Huang et al., 2010; Miteni, 2013), in unknown amounts.

Because the production processes for PBSF/PHxSF (through ECF) are similar to those of POSF-based products (Gramstad and Haszeldine, 1957), it is expected that PFCA s are formed as impurities during the production of PBSF/PHxSF; part of the PFCA impurities can react with the reactants added in the subsequent reactions of PBSF/PHxSF and form derivatives such as perfluoroalkane carboxamides ($C_nF_{2n+1}CONH(R)$, $R = CH_3$ or C_2H_5) (Jackson and Mabury, 2013). Similar to their C_8 homologues, these PFCA impurities can be released during the product life-cycle of PBSF/PHxSF-based products. In addition, PFCA derivatives (Jackson et al., 2013; Seacat, 2004) and PBSF/PHxSF-based substances (Martin et al., 2010) can degrade into PFCA s in the environment and biota. Therefore, PBSF/PHxSF-based products act as direct and indirect sources of PFCA s to the environment.

Semifluorinated alkanes [SFAs, $F(CF_2)_n(CH_2)_mH$, often denoted as F_nH_m] act as an additional source of PFCA s. The short-chain SFAs (with chain lengths up to 14 carbons) are used in various medical applications (as components of artificial blood, in drug delivery and in ophthalmology as so-called endotamponades in complicated vitreoretinal surgery; Broniatowski and Dynarowicz-Łątka, 2008), whereas the long-chain SFAs (≥ 22 carbons) have been applied in ski waxes since the 1990s (Buck et al., 2011; Freberg et al., 2010; Plassmann and Berger, 2010; Plassmann et al., 2011). Various short-chain SFAs (e.g., F_6H_6 , CAS No. 69125-80-0; F_6H_8 , CAS No. 133331-77-8; F_8H_8 , CAS No. 6145-05-7) have been produced by (at least) Fluoron in Germany and Fuxin Hengtong in China (Fluoron, 2014; Fuxin, 2014), whereas there is no information on production of long-chain homologues. Recently, PFCA s were detected in SFA-containing ski waxes (Plassmann and Berger, 2010). Since SFAs are derived from perfluoroalkyl iodides (PFAIs) (Buck et al., 2011; Krafft and Riess, 2009), PFCA s occurring in SFAs can (partly) be impurities from the production of the parent compounds (PFAIs) (Larsen et al., 2006; Telomer Research Program, 2003). In addition, SFAs might degrade into PFCA s under certain conditions; one homologue, CF_3CH_3 , has been shown to react with OH radicals to give $CF_3CH_2O_2\cdot$ radicals. The $CF_3CH_2O_2\cdot$ radicals can further react with NO and O_2 and form CF_3CHO (Nielsen et al., 1994), which is a known precursor of CF_3COOH (Hurley et al., 2006). In general, however, formation of PFCA s from SFAs still needs to be proven by further research. It is currently not possible to estimate PFCA emissions from SFAs, because there is no information on the historical production of SFAs, in addition to their uncertain degradation. We expect, however, that PFCA emissions resulting from the life-cycle of SFA-containing ski waxes are of minor global importance because, due to their high cost, these ski waxes are sold in relatively low amounts.

Furthermore, 3M produced 7:1 FTOH ($C_7F_{15}CH_2OH$, CAS No. 307-30-2), which was used to produce (at least) two acrylate and methacrylate monomers (L-9186, $C_7F_{15}CH_2OC(O)CH=CH_2$, CAS No. 307-98-2; L-9187, $C_7F_{15}CH_2OC(O)C(CH_3)=CH_2$, CAS No. 3934-23-4, see Fig. 2), as

indicated in Chapter 27 of Banks et al. (1994). The polymers based on these acrylic ester monomers were likely used as oil- and water-repellent finishes for textiles (Bryce, 1964; Holzapfel, 1966; Scherer, 1970) and as coatings in electronic applications to provide a humidity barrier on printed circuit boards and to secure silicone oil on precision bearings (3M, 2000c, 2003). In 2000–2002, 3M ceased its global production of 7:1 FTOH along with its phase-out of other long-chain PFAS (3M, 2000a, 2003). Recently, Miteni started to produce the shorter-chain homologues, 3:1 and 5:1 FTOHs, $C_nF_{2n+1}CH_2OH$, $n = 3, 5$, CAS Nos. 375-01-9 and 423-46-1, which may have been used as building blocks for side-chain fluorinated polymers in unknown amounts (Miteni, 2013). These n :1 FTOHs are likely produced through catalytic hydrogenation of the corresponding PFCA s (e.g., $C_5F_{13}COOH \rightarrow C_5F_{13}CH_2OH$) (Husted and Ahlbrecht, 1954). Hence, some PFCA s may remain as unreacted residuals in these n :1 FTOHs. In addition, studies have shown that n :1 FTOHs can undergo OH-radical-mediated oxidation and form the corresponding aldehydes (Hurley et al., 2004), $F(CF_2)_nCHO$, which can be further oxidized and form PFCA s (Hurley et al., 2006). The rate constant for the reaction of 3:1 FTOH with OH radicals has been measured in laboratory experiments (see Table 3). It has been suggested that this rate constant is largely independent of the perfluoroalkyl chain length and, therefore, is also valid for other n :1 FTOHs (Bravo et al., 2010; Hurley et al., 2004). Note that the starting materials of n :1 FTOHs, which are likely to be PFCA s, are produced by electrochemical fluorination; therefore, n :1 FTOHs and PFCA residuals therein consist of both linear and branched isomers (Missio and Bertola, 2010).

3. Can (bio)degradation of side-chain fluorinated polymers be a relevant source?

In this section, we perform bounding calculations to evaluate if (bio) degradation of side-chain fluorinated polymers can be a relevant source of PFCA s. We run scenario calculations in which we investigate the influence of two key parameters, namely: [i] degradation half-life and [ii] product lifetime of polymeric products. In general, we assume that all polymeric species in products (bio)degrade continuously during the product lifetime with a first-order rate constant derived from the degradation half-life assumed in each scenario. After the end of their lifetime, the products are assumed to be properly treated (i.e., safely landfilled or incinerated) and no longer available for degradation to form PFCA s.

We investigate different scenarios with various degradation half-lives and lifetimes of polymeric products and estimate the corresponding emissions of perfluorooctane sulfonamides/sulfonamido ethanols (xFOSEA/Es) and 6:2–14:2 FTOHs from (bio)degradation of relevant side-chain fluorinated polymers. Then, we compare these estimated emissions from (bio)degradation of side-chain fluorinated polymers to our previous estimates of xFOSEA/Es and 6:2–14:2 FTOHs from all other sources (including as ingredients, as residuals in products, as degradation products of certain non-polymeric substances) as reported in the companion paper (Wang et al., 2014). For xFOSEA/Es this comparison is shown in Fig. 3 and for 6:2–14:2 FTOHs it is shown in Fig. 4. We do not include 4:2 FTOH, because 4:2 fluorotelomer-based raw materials are mainly used as (co)monomers in the manufacture of certain fluoropolymers and fluorinated silicone polymers (DuPont, 2008; Telomer Research Program, 2002).

The eight scenarios illustrated in Fig. 3 show that longer product lifetime leads to higher releases of PFCA precursors. This is due to larger amounts of POSF- and fluorotelomer-based polymers that accumulate in various products, goods and materials during the lifetime of these products and are available for degradation and, second, due to a longer period of time during which degradation of side-chain fluorinated polymers occurs. Additionally, a shorter degradation half-life also results in higher releases of potential PFCA precursors. Among the eight scenarios, the scenario with a short product lifetime (5 years) and a long degradation half-life (100 years) represents a reasonable low-release scenario

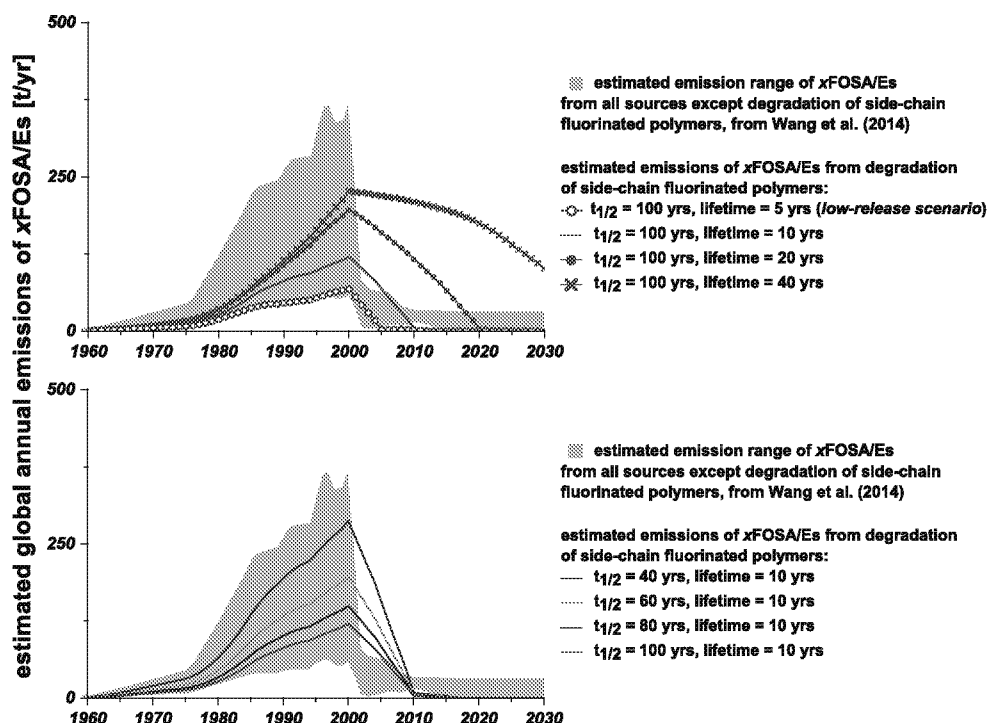


Fig. 3. Blue area: estimated global annual emissions of xFOSEs from all sources except degradation of POSF-based side-chain fluorinated polymers (from Wang et al. (2014)). Lines: hypothetical emissions of xFOSEs from degradation of POSF-based side-chain fluorinated polymers (top: constant degradation half-life ($t_{1/2}$) and different product lifetimes; bottom: constant product lifetime and different degradation half-lives).

of PFCA precursors from degradation of side-chain fluorinated polymers (Figs. 3 and 4).

Even in this low-release scenario, the estimated emissions of xFOSEs from (bio)degradation of side-chain fluorinated polymers are still considerable in comparison to the emission estimates from all other sources as reported by Wang et al. (2014) (Fig. 3, top). Similarly, the estimated emissions of FTOHs are all in the range of the emission estimates from all other sources (see Fig. 4). Hence, (bio)degradation of side-chain fluorinated polymers can be an additional significant source particularly for some PFCA homologues (such as C_7 , C_{12} and C_{14} PFCA) that were mainly emitted as degradation products of precursors in our previous estimates (see Fig. 4 in the companion paper, Wang et al., 2014). It should be noted that the above calculations are based on the assumption that at the end of the product lifetime all side-chain fluorinated polymers were treated (incinerated and landfilled) and thus no longer active as PFCA sources. In reality, when side-chain fluorinated polymers are landfilled, they might still undergo (bio)degradation and form PFCA precursors in landfills, which can enter the environment through volatilization (Ahrens et al., 2011) or in leachate (Benskin et al., 2012; Busch et al., 2010; Huset et al., 2011). Therefore, for a more realistic assessment, the understanding of the mass flow of side-chain fluorinated polymers during their whole life-cycle, including in landfills, needs to be improved.

4. Outlook

PFCA with four or more carbons are a group of global contaminants of concern that have no natural origins. After over a decade of research, four important sources are relatively well understood; these include PFCA releases from the life-cycle of PFOA-, PFNA-, POSF- and fluorotelomer-based products in industrial and urban areas, including households and waste treatment facilities. In spite of remaining uncertainties associated with some of these sources, a reasonable

estimation of PFCA releases from these sources on a global scale is possible, see Wang et al. (2014). However, the understanding of some PFCA sources is still incomplete, particularly for the short-chain homologues. In this study, we have identified eleven additional sources of PFCA emissions. Currently there is insufficient knowledge in the public domain to perform a quantitative assessment of historical and current PFCA releases from these sources. However, our work reveals that some of the sources may have been significant in the past, such as historical use and release of C_4 – C_7 PACF- as well as C_4 – C_7 and C_{10} PASF-based products, whereas other sources can be significant and long-lasting, such as the slow but continuous atmospheric transformation of HFCs and HFES as well as (bio)degradation of POSF- and (n:1 and n:2) fluorotelomer-based side-chain fluorinated polymers. Furthermore, some sources (e.g., branched PFNA-based products, HFES and n:1 FTOHs) can contribute to branched PFCA in the environment and influence the ratios of linear and branched PFCA isomers in certain regions. Other sources (e.g., HFE-7100 in personal care and cosmetic applications) can lead to new human exposure routes to PFCA that have not yet been considered in previous studies. We conclude that a better understanding of these remaining pieces of the PFCA emission puzzle is needed to quantitatively describe the levels and trends of C_4 – C_{14} PFCA homologues in the environment and to characterize the environmental and human exposure to these chemicals. To fill the critical knowledge and data gaps (see Table 1) and to work towards a comprehensive global emission inventory of C_4 – C_{14} PFCA homologues, more efforts are still needed, including improved cooperation between scientists in academia, industry and government institutions. Future work should include [i] retrospective assessment of PFCA releases from historical use of PFCA-related products with necessary input regarding their production history from industry; [ii] development of effective methods for measuring or estimating degradation half-lives of various HFCs, HFES, and side-chain fluorinated polymers; and [iii] investigation of PFCA releases from current use of PFCA-related products, particularly from those that

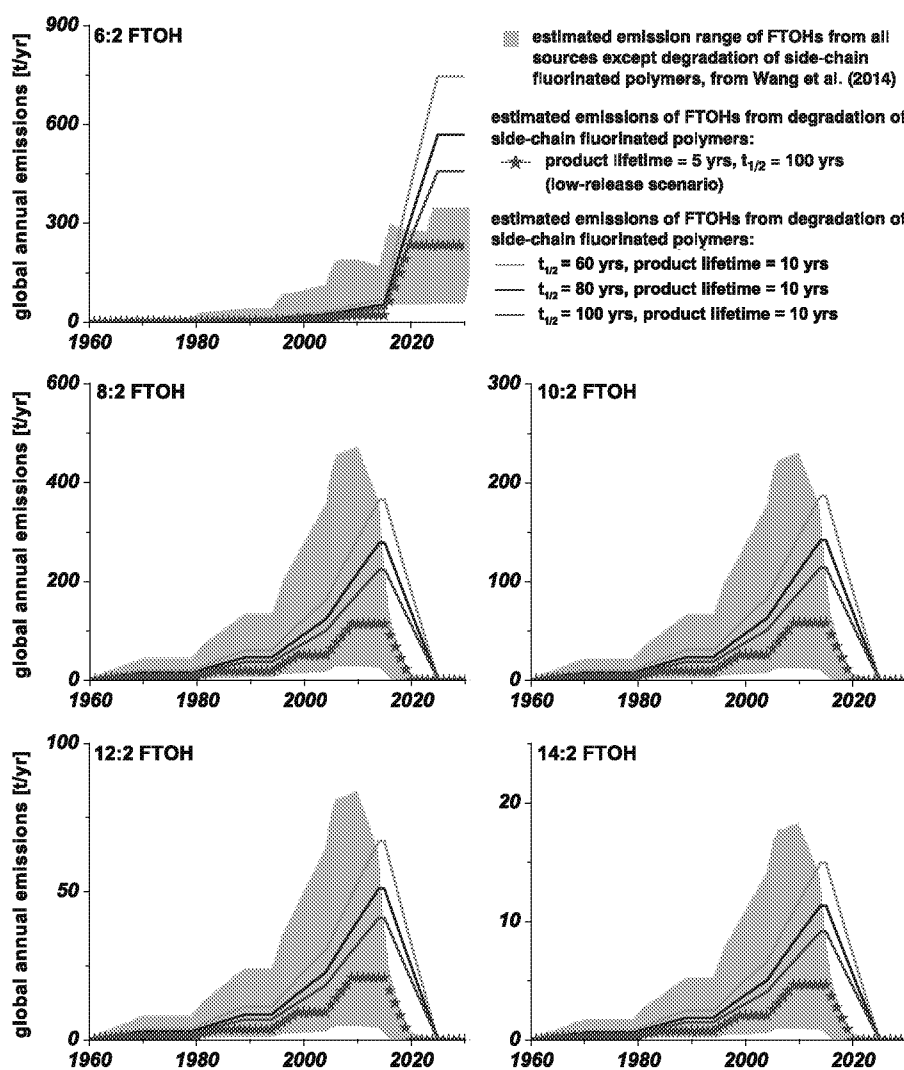


Fig. 4. Blue area: estimated annual emissions of 6:2–14:2 FTOHs from all other sources except degradation of fluorotelomer-based side-chain fluorinated polymers (from Wang et al. (2014)). Colored lines: hypothetical emissions of 6:2–14:2 FTOHs from degradation of side-chain fluorinated polymers under different conditions.

are developed as replacements of long-chain PFCAs and their precursors, in order to prevent emissions from occurring on a large scale.

Conflict of interest

R. C. Buck is an employee of E. I. duPont de Nemours and Company, Inc., a global manufacturer of fluoropolymers and fluorotelomer-based products.

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